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Procedia Engineering 25 (2011) 1429 – 1432

Procedia Engineering

www.elsevier.com/locate/procedia

Proc. Eurosensors XXV, September 4-7, 2011, Athens, Greece

Faster response times of rare-earth oxycarbonate based CO_2 sensors and another readout strategy for real-world applications

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Abstract

The contribution presents the results of investigations performed on the new class of CO_2 chemoresistive materials based on rare earths oxy-carbonates. Firstly, the performance an alternative sensor readout parameter, work function, is presented together with a comparison between the effect of the target gas, CO_2, and main interferent, water vapor. Afterwards, new synthesis routes, targeting the lowering of the sensitive materials costs are described together with sensing performance obtained in realistic application conditions.

Keywords: CO_2 gas sensor, chemoresistive, workfunction, Rare earth oxy carbonate, response time

1. Introduction

CO_2 gas sensing plays a key role for different important sensing application. One application is indoor air quality monitoring. Unfortunately, all commercially available CO_2 sensors are both expensive and difficult to use. The high cost and difficult device implementation hinders their wide market adoption and development of new applications and devices. The possible demand for cheap and easy to use CO_2 gas sensors drives our research in this area. In our previous work we have shown that chemoresistive sensors

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1877-7058
doi:10.1016/j.proeng.2011.12.353

based on Neodymium-oxy-carbonate exhibit large resistance changes under CO_2 exposure and we demonstrated, by using operando DRIFT spectroscopy, that the sensing mechanism is related to the interaction between the target gas and surface hydroxyl groups [1,2]. We also demonstrated that the CO_2 sensing is linked to the oxy-carbonate phase and it is lost after the conversion to the oxide: the Lanthanum† oxy-carbonate has even higher sensor signals then the Neodymium but the Praseodymium, which forms the oxide phase, does not show sensing effects [3].

There are also disadvantages associated to the new class of sensing materials: very large sensor resistances, slow response and recovery times, high costs of the precursors. In this contribution we address some of the major drawbacks, namely we are looking to work function changes as an alternative sensor readout, we are examining a different synthesis route and we examining the impact on the response/recovery times of application-like testing conditions.

2. Work function readout

Lately, platforms that are able to major work function changes of gas sensitive materials became commercially available [4]. To assess the possibility of using such platforms, work function measurement were performed with a McAllister Kelvin Probe 6500; for a detailed presentation of the method, see [5]. In those experiments, a Lanthanum-oxy-carbonate ($La_2O_2CO_3$) based sensing layer, deposited on an alumina substrate provided with electrodes and heater, was used; the synthesis route is presented in [3]. All measurements were performed at 300°C: Figure 1 shows the work function changes (Contact Potential Difference CPD) under exposure to five 2.5 hours pulses of different humility levels (5% to 25%) in a dry atmosphere background, blue line, and also the work function changes under exposure to five 2.5 hours pulses of different CO_2 concentrations (300 to 500ppm) in a humid atmosphere (25% r.h.) background, red line.

One can see that the CPD is increasing upon humidity exposure. As the CPD is inverse connected to the work function change, the work function itself is decreasing. The reactivity of the material towards humidity gets saturated near 15% relative humidity, which is positive because for indoor applications r h. level of 15% can be expected.

For the case of CO_2 exposure, the opposite work function effect is visible as the CPD is decreasing. To compare the results of humidity and CO_2 exposure, the values of the maximal CPD change at the end of each target gas exposure period are shown in Figure 2. One can easily see that the signals are quite large and it is perfectly possible to distinguish between 300ppm, which is the background value in the atmosphere, and 100ppm, which is a significant target value in indoor air quality.

To be able to transfer the measurements on the commercial platforms, one needs to further decrease the operation temperature.

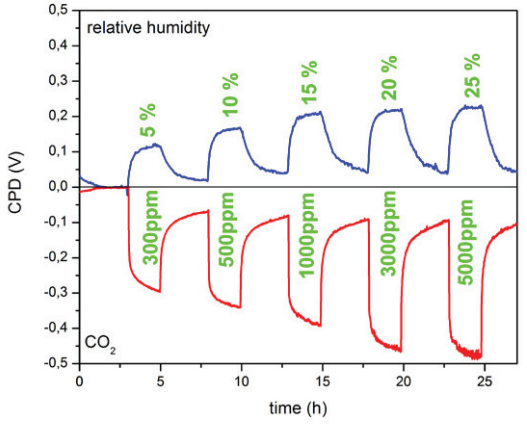

Fig 1: Kelvin Probe Measurements of $La_2O_2CO_3$ for different humidity and CO_2 concentrations.

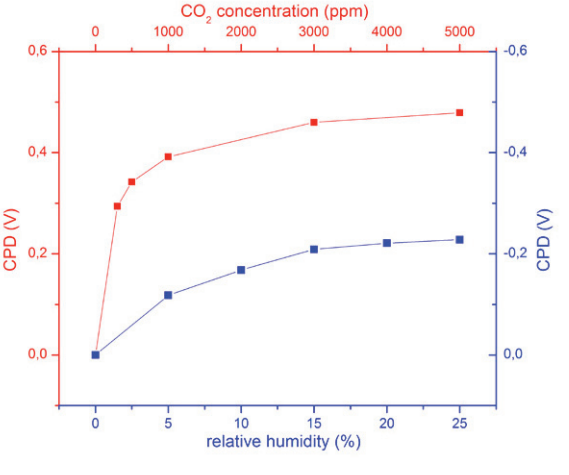

Fig. 2: Comparison of CPD changes for different humidity and CO_2 concentrations.

3. New material synthesis and response times,

As the precursor materials for the original synthesis presented in [1] are difficult to acquire and costly because of its intrinsic chemical energy, a different synthesis route was investigated: stirring of La_2O_3 in warm water for 6h and a consecutive stirring in cold water. The sensing performance investigations indicate that the as-obtained sensing layer is much more conductive than the ones synthesized before. The measurement results performed at 50% r.h. and as an operation temperature of 300°C are plotted in Figure 3; the baseline resistance lies now around 300MOhm. Two type of exposures were applied in order to investigate the origin of the low response/recovery times: 1h pulses of 350ppm, 1000ppm and 3000ppm CO_2 and a staircase ramp. The sensor signals are very high, reaching up to a factor 20 in the case of exposure to 3000ppm CO_2. The ramp measurement shows, that the recovery time in the ramp is much faster than the initial response time, which indicates that by equilibrating the sensor in a background of a low concentration of CO_2 – like in the case of real applications, the problem can be avoided.

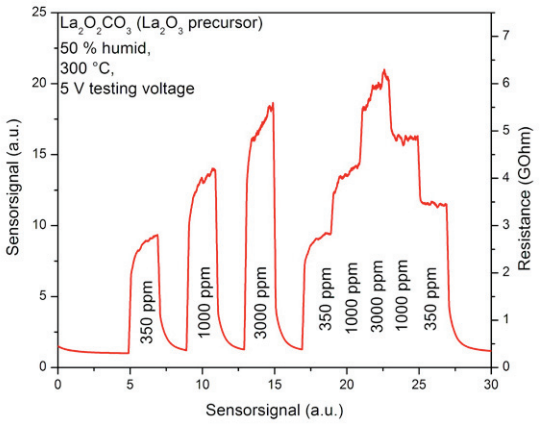

Fig. 3: Time dependence of the sensor resistance under CO_2 exposure in humid, synthetic air. The recovery time of the ramp is much faster than the recovery in CO_2 lean conditions.

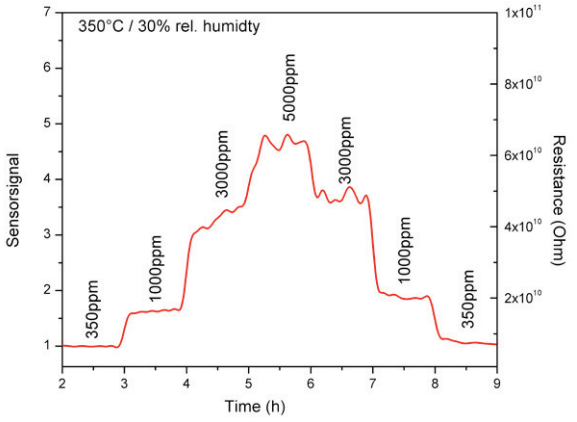

Fig. 4: Resolution of different CO_2 concentrations in a background of 350ppm CO_2. The sensor can still differentiate between concentrations up to 5000ppm. The response time lies in a few minutes.

To check this idea, a measurement at 350°C and 30% relative humidity was performed: the important difference is that the background also contained 350ppm CO_2, as it would be typically found in the ambient atmosphere. The results indicate that the response/recovery times are significantly decreased

when compared to the measurements performed in CO_2 free backgrounds. This suggests that the sensing process is split in two different mechanisms: One for a pre-equilibration up to 350ppm and another for higher concentrations. For real world application this is an important finding, as fast response is a key for many applications. The resistance of the material is still very high, which makes it still expensive to implement these materials into sensors. At the moment we are investigating methods to reduce the sensor resistance to even lower baselines, while keeping the high sensor signals.

4. Conclusion and outlook

We presented alternative solutions for the disadvantages of the new class of CO_2 chmoresistive materials based on rare earths oxy-carbonates: work function measurement on $La_2O_2CO_3$ as an alternative read out; cheaper ways to synthesize the materials; investigation of the effect of CO_2 containing backgrounds on sensor response/recovery times. The findings are very encouraging and point out to the future development work: decrease of the operation temperature; finding of technological strategies for the further decrease of sensor resistance.

Acknowledgements

A.H., N.B. and U.W. are thankful to DFG for the support provided through WE 3662/4-1– „SESAM“.

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